



Photocatalytic hydrogen formation from ammonia and methyl amine in an aqueous suspension of metal-loaded titanium(IV) oxide particles

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ABSTRACT

Photocatalytic hydrogen (H_2) formation from ammonia and methyl amine in aqueous suspensions of metal-loaded titanium(IV) oxide (TiO_2) particles was examined under various conditions. Ammonia was decomposed to H_2 and nitrogen (N_2) with a stoichiometric ratio ($3:1, 2NH_3 \rightarrow 3H_2 + N_2$) under a deaerated condition, and side reactions such as deep oxidation of ammonia to nitrite and nitrate did not occur. The rate of H_2 formation drastically changed depending on the co-catalyst loaded on TiO_2 particles, kinds of TiO_2 samples and pH of the suspension. The effect of the co-catalyst became greater with decrease in hydrogen over-voltage, the value of which was obtained when the co-catalyst metal was used as an electrode. Among the co-catalysts used in this study, platinum showed the greatest effect as a co-catalyst. The largest rate of H_2 evolution was obtained when the photocatalytic reaction was carried out at pH 10.7, and addition of an acid or base to the suspension decreased the reaction rate. Photocatalytic reaction of methyl amine in aqueous suspension of platinized TiO_2 particles under a deaerated condition yielded H_2 but did not form N_2 . The methyl group of methyl amine was mineralized and the amino group remained as ammonium ion without being decomposed to H_2 and N_2 , resulting in storage of carbon as hydrogencarbonate (HCO_3^-) in the suspension. Photocatalytic reaction of methyl amine under the present conditions was totally expressed as $CH_3NH_2 + 3H_2O \rightarrow 3H_2 + NH_4^+ + HCO_3^-$.

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1. Introduction

Water splitting to produce hydrogen (H_2) using solar energy has been considered as one of the most important approaches to solving the world energy problem. Semiconductor photocatalysts that decompose water to H_2 and oxygen (O_2) (Eq. (1)) have been extensively investigated and various kinds of photocatalysts have been reported [1–14].

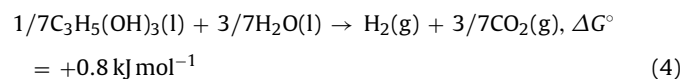
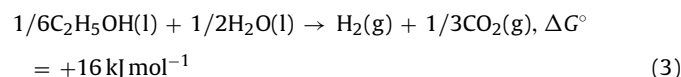


However, the positively large standard Gibbs free energy change ΔG° of 237 kJ mol^{-1} means that water splitting is an uphill reaction and requires large energy to obtain products (H_2 and O_2). In addition to thermodynamical difficulty, most of the metals that have been used as a co-catalyst of the water splitting photocatalyst often work as a thermocatalyst for the reverse reaction (Eq. (2)).



Other photocatalytic H_2 formations from biomass alcohols such as ethanol (Eq. (3)) and glycerol (Eq. (4)) in aqueous solutions under

a deaerated condition, in which alcohols act as hole scavengers and protons are reduced to H_2 by photogenerated electrons, have also been studied [15–22].



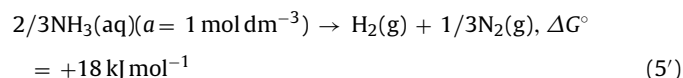
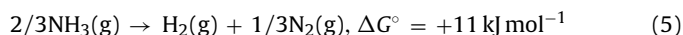
Reactions of H_2 formation from alcohols apparently have thermodynamical advantages compared with water splitting. For example, values of ΔG° of H_2 formation from ethanol and glycerol are calculated to be 16 and 0.8 kJ mol^{-1} , respectively, assuming that ethanol and glycerol are completely decomposed to carbon dioxide. The values are less than one-tenth of that of water splitting. Reverse thermal reaction between H_2 and carbon dioxide (CO_2) is kinetically negligible at room temperature under almost atmospheric pressure, indicating that H_2 formation reactions from alcohols are more kinetically favorable than water splitting. Therefore, photocatalytic H_2 formation from biomass alcohols is one of the important practical candidates that enable us to produce H_2 continuously. However, since incomplete mineralization of alcohols

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may cause contamination of water with unfavorable intermediates in photocatalytic reaction, the depth of the alcohol oxidation should also be evaluated as well as H_2 formation. In addition, a tight supply–demand situation for food by the use of alcohols as hydrogen sources in the photocatalytic reaction should be avoided. Under these circumstances, biomass wastes are promising candidates as hydrogen sources in the photocatalytic reaction because biomass wastes cause no tight supply–demand situation for food.

Ammonia (NH_3) and related compounds such as methyl amines are typical biomass wastes that are mainly included in excretions. A large amount of NH_3 is industrially produced and is used as important starting materials of chemicals, medicines, fertilizers and agrichemicals. Most of the NH_3 used in chemical plants is effectively recovered, whereas recovery of other NH_3 fixed in medicines, fertilizers and agrichemicals is almost impossible. Formation of H_2 by decomposition of NH_3 (Eqs. (5) and (5')) is more thermodynamically advantageous than water splitting.



Moreover, H_2 formation from NH_3 means its detoxication to nitrogen (N_2). The reverse reaction (production of NH_3) does not occur at room temperature and under atmospheric pressure because this reaction requires a high pressure and high temperature to obtain a sufficient reaction rate. Therefore, NH_3 is one of promising candidates working as a hole scavenger for photocatalytic H_2 formation. However, to our knowledge, there are no reports on photocatalytic H_2 formation from NH_3 and parameters affecting the reaction rate. In this study, we examined photocatalytic decomposition of NH_3 and methyl amine in aqueous suspensions of metal-loaded titanium(IV) oxide (TiO_2) particles. Here we report (1) photocatalytic H_2 evolution from NH_3 in an aqueous solution, (2) effects of metal co-catalysts, reaction conditions and physical properties of TiO_2 , and (3) photocatalytic H_2 formation from methyl amine and its degradation behavior.

2. Experimental

2.1. Materials and catalyst preparation

All chemicals were used without further purification. In most of the experiments, Degussa P25 TiO_2 was used. To investigate the effect of physical properties of TiO_2 , TiO_2 powder was synthesized by using the HyCOM method [23,24], which is one of the solvothermal methods: titanium(IV) butoxide (25 g) in toluene (70 cm^3) was heated at 300 °C for 2 h in an autoclave in the presence of water (10 cm^3) fed in a space separated from alkoxide solution. The resulting powder was washed repeatedly with acetone and dried in air at ambient temperature. The HyCOM TiO_2 powder was calcined at various temperatures in a box furnace for 1 h to change the physical properties in a wide range. In some of the experiments, TiO_2 samples supplied from The Catalysis Society of Japan (reference catalyst, JRC-TIO series) were also used.

Photodeposition was used to load various metals on TiO_2 and chloride (or sulfate) was used as the metal source. Bare TiO_2 particles (297 mg) were suspended in an aqueous solution (15 cm^3) containing a metal source (0.1 wt% as metal) and sodium oxalate (300 μmol) and were photoirradiated for 2 h with a 400 W high-pressure mercury arc ($\lambda > 300 \text{ nm}$, Eiko-sha, Japan) with magnetic stirring (1000 rpm) under argon (Ar) at 25 °C. Analysis of the liquid phase after photoirradiation revealed that all metals were deposited on the TiO_2 particles as charged. After irradiation, the

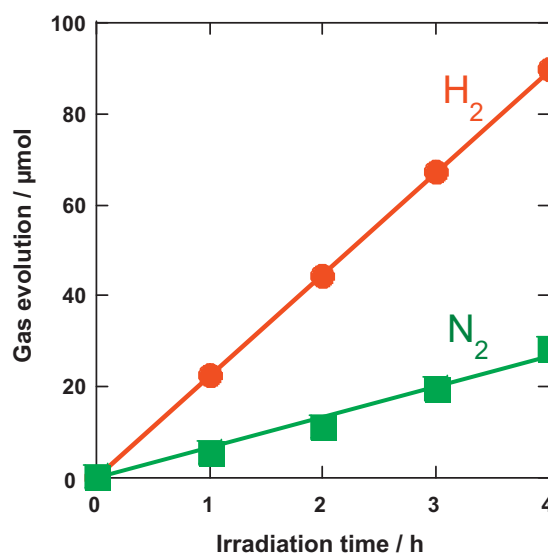


Fig. 1. Photocatalytic decomposition of ammonia (500 μmol) in an aqueous suspension of platinum-loaded TiO_2 (P25) particles.

TiO_2 particles were recovered, washed repeatedly with water, and dried at 20 °C *in vacuo* for 2 h.

2.2. Photocatalytic reaction

Bare or metal-loaded TiO_2 particles (50 mg) were suspended in an aqueous solution (5 cm^3) containing NH_3 (500 μmol , Kanto Chemicals) in a test tube. If necessary, pH of the suspension was adjusted to the desired value using sodium hydroxide solution or sulfuric acid. The tube was sealed with a rubber septum and then photoirradiated at $\lambda > 300 \text{ nm}$ with the same mercury arc under Ar of 1 atm with magnetic stirring (1000 rpm) in a water bath continuously kept at 25 °C. In the case of decomposition of methyl amine, methyl amine (30 μmol , Kanto Chemicals) was injected into the aqueous suspension of metal-loaded TiO_2 particles in the test tube through the rubber septum. The amounts of N_2 , H_2 and O_2 in the gas phase of reaction mixtures were measured using a Shimadzu GC-8A gas chromatograph (GC) equipped with an MS-5A column. In the case of decomposition of methyl amine, the amount of CO_2 in the gas phase was measured using another GC equipped with a Porapak Q column. Concentrations of nitrate (NO_3^-) and nitrite (NO_2^-) in the liquid phase were determined with a Jasco PU-2800 plus ion chromatograph (IC) equipped with an ICNI-424 column (Shodex, Japan). Concentrations of NH_3 (in the form of NH_4^+) in the liquid phase were determined with a TOA Electronics LASA-20 spectrophotometer.

3. Results and discussion

3.1. Photocatalytic decomposition of ammonia in an aqueous suspension of platinum-loaded TiO_2 particles

H_2 was not formed from an aqueous suspension of platinumized TiO_2 (P25) in the absence of NH_3 , indicating that photocatalytic water splitting (Eq. (1)) did not occur or that the reverse reaction (Eq. (2)) occurred very rapidly under the present conditions in which the gas phase in the glass tube (reactor) was initially filled with Ar of 1 atm. Fig. 1 shows time courses of evolutions of H_2 and N_2 in photocatalytic decomposition of NH_3 in an aqueous suspension of platinum-loaded TiO_2 (P25) particles. As expected from the thermodynamical consideration, H_2 and N_2 were evolved just after photoirradiation, in contrast to the results for pure water. After

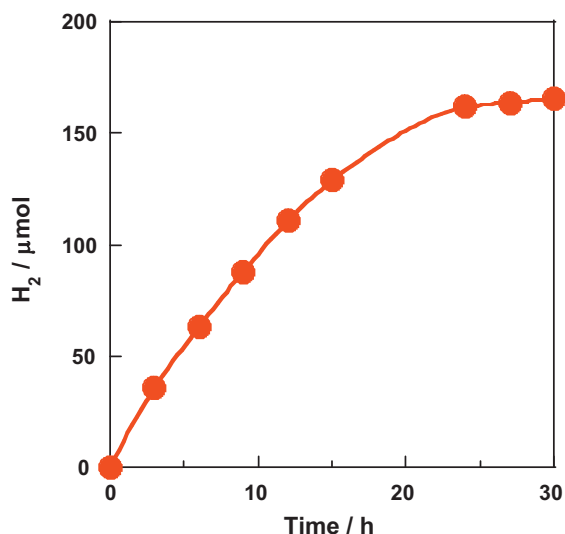


Fig. 2. Photocatalytic formation of H₂ from ammonia (107 μmol) in an aqueous suspension of platinum-loaded TiO₂ (P25) particles.

photoirradiation for 4 h, the amounts of H₂ and N₂ reached 90 and 28 μmol, respectively, and the H₂/N₂ ratio was 3.2, which was in agreement with the stoichiometry of NH₃ decomposition (Eq. (5)) within the experimental error. Formation of O₂ was negligible, indicating that water splitting in the presence of NH₃ did not occur. The amounts of NO₃[−] and NO₂[−] in the liquid phase were under the detection limit of ion chromatography. These results indicate that deep oxidation of NH₃ generally observed in the photocatalytic reaction in the presence of O₂ did not take place under the present conditions. Therefore, these experimental data show that decomposition of NH₃ occurred easily compared with water splitting and that NH₃ was decomposed to H₂ and N₂ stoichiometrically without side reactions. Fig. 2 shows time course of evolutions of H₂ in photocatalytic decomposition of NH₃ (107 μmol) in an aqueous suspension of platinum-loaded TiO₂ (P25) particles. Formation of H₂ was saturated at around 160 μmol, although the reaction rate was smaller than that shown in Fig. 1 (500 μmol of NH₃) due to the smaller amount of NH₃. The H₂ yield (160 μmol) was in good agreement with the amount of NH₃ (107 μmol), indicating a high stoichiometry of decomposition of NH₃ to H₂.

3.2. Effects of co-catalyst loaded on TiO₂ particles and pH of the suspension containing ammonia

Various co-catalysts were loaded on TiO₂ (P25) and used for photocatalytic decomposition of NH₃ in the aqueous suspension. It is known that a co-catalyst such as Pt loaded on a photocatalyst acts as a site for storage of photogenerated electrons and as an active site, resulting in decrease in activation energy of the reaction and formation of a reduced product [22,25]. The rate was drastically changed depending on the type of co-catalyst, and Pt had the greatest effect as a co-catalyst. As shown in Fig. 3, the effect as a co-catalyst became smaller with increase in hydrogen over-voltage of the co-catalyst metal when used as an electrode [26], suggesting that reduction of protons by photogenerated electrons in the conduction band of TiO₂ is the rate-determining step in this reaction system under the present conditions.

Fig. 4 shows the effect of pH of the suspension on the rate of H₂ formation. The largest rate of H₂ evolution was obtained when the photocatalytic reaction was carried out at pH 10.7 with neither an acid nor a base being added to the suspension. The rate slightly decreased with increase in pH of the suspension with NaOH solution. The decrease in solubility of NH₃ in water in the

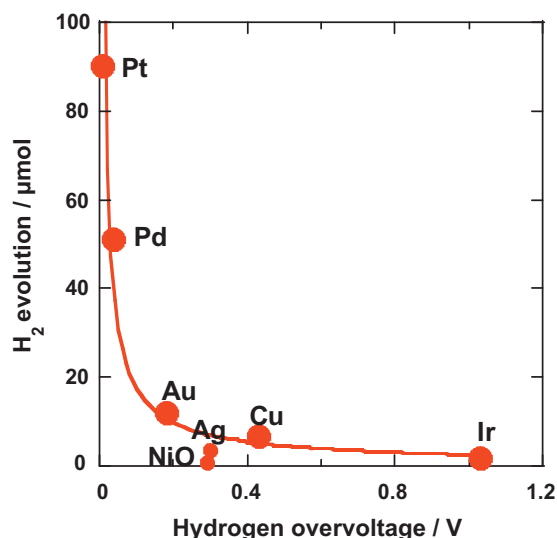


Fig. 3. Correlation between photocatalytic H₂ evolution for 4 h from ammonia (500 μmol) in an aqueous suspension of metal-loaded TiO₂ (P25) particles and hydrogen overvoltage of metal electrodes.

presence of a strong base is attributed to decrease in the reaction rate. The formation rate also decreased with decrease in pH of the suspension with sulfuric acid. Addition of acid causes protonation of NH₃, resulting in formation of ammonium ion (NH₄⁺). Since the isoelectric point of TiO₂ particles is generally observed at around pH 6, the surface of TiO₂ particles in the suspension is negatively charged at pH > 6. Therefore, the amount of NH₄⁺ adsorbed on the TiO₂ surface would increase; however, the amount of evolved H₂ decreased, suggesting difficulty in photocatalytic decomposition of NH₄⁺ adsorbed. Evolution of H₂ was almost completely suppressed at pH < 6 due to the large decreases in both the amount of NH₃ in the liquid phase and the amount of NH₄⁺ adsorbed on the TiO₂ surface positively charged. Time course of evolutions of H₂ in photocatalytic decomposition of NH₃ (107 μmol) in an aqueous suspension of platinum-loaded TiO₂ (P25) particles was shown in Fig. 2. The reaction rate gradually decreased with progress in NH₃ decomposition. This result is explained by two reasons, i.e. the decrease in the amount of NH₃ adsorbed on the TiO₂ surface

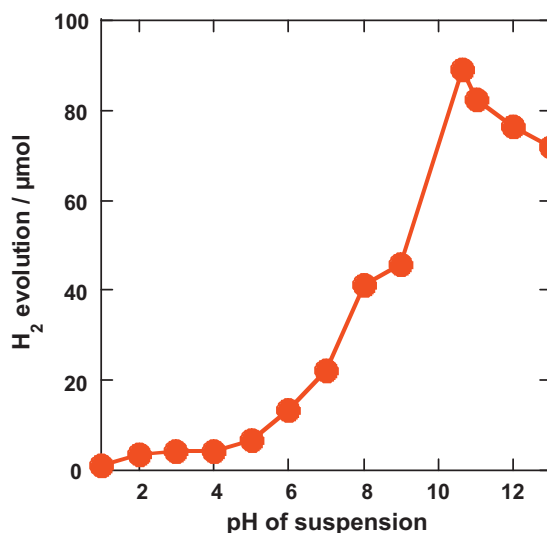


Fig. 4. Effect of pH of the suspension on photocatalytic H₂ formation for 4 h from ammonia (500 μmol) in an aqueous suspension of platinum-loaded TiO₂ (P25) particles.

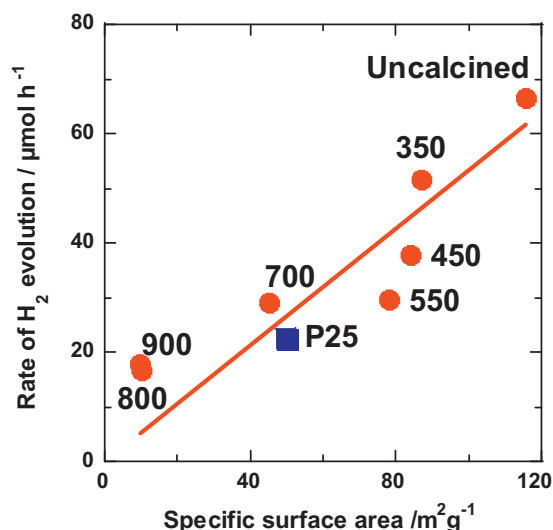


Fig. 5. Effects of specific surface areas of various HyCOM TiO₂ samples (circles) and P25 TiO₂ (square) on photocatalytic H₂ evolution from ammonia (500 μmol) in aqueous suspensions of platinized TiO₂ samples. Specific surface area of HyCOM TiO₂ was changed by calcination, and the temperatures in Celsius are shown in the figure.

and the decrease in pH of the suspension due to consumption of NH₃.

3.3. Effect of physical properties of TiO₂

To investigate the effect(s) of physical properties of TiO₂, HyCOM TiO₂ samples uncalcined and calcined at various temperatures were platinized and used for photocatalytic decomposition of NH₃. Physical properties of anatase-type HyCOM TiO₂ can be changed in a wide range by calcination, and the effects of physical properties on photocatalytic performance were examined free from the effects of phase transfer to the rutile form and contaminants such as sulfate and chloride ions originating in starting materials [27–34]. The specific surface area of HyCOM TiO₂ was changed from 116 m² g^{−1} (sample uncalcined) to 9.7 m² g^{−1} (sample calcined at 900 °C). Fig. 5 shows results of photocatalytic H₂ evolution from NH₃ in aqueous suspensions of these HyCOM TiO₂ samples loaded with Pt. A linear correlation between photocatalytic performance and specific surface area of HyCOM TiO₂ samples was observed, indicating that surface area of TiO₂ is one of the important factors controlling the photocatalytic activity in H₂ evolution from NH₃ in an aqueous suspension. In previous studies, we found that physical properties of TiO₂ affected photocatalytic activities in different ways depending on the type of photocatalytic reaction [27,28,30,32,33]. In dehydrogenation of 2-propanol, which has often been used as a model reaction to evaluate photocatalytic activity for H₂ formation, HyCOM TiO₂ calcined at around 700 °C, in which the specific surface area (SSA) and the crystallinity were well balanced, exhibited the highest activity and samples satisfying only either large SSA or high crystallinity showed lower activities [27,33]. These results suggest that physical properties of TiO₂ affected photocatalytic activities in different ways depending on the type of substrate in the H₂ evolution system. Although P25 TiO₂ was produced by another method, i.e. gas-phase decomposition of titanium chloride, SSA of P25 TiO₂ was similar with that of the HyCOM sample calcined at 700 °C. As shown in Fig. 5, the photocatalytic performance of P25 TiO₂ was similar to that of the HyCOM sample calcined at 700 °C. It is interesting that photocatalytic activity of commercial TiO₂ was included in the same activity–SSA correlation of the series of HyCOM TiO₂ samples.

Table 1

Particle size and specific surface area of JRC-TiO samples.

JRC-TiO	Crystalline phase by XRD ^a	Particle size ^b (nm)	S _{BET} ^c (m ² g ^{−1})
4	A, R	21	58
6	R	15	105
7	A	8	302
8	A	– ^d	314
9	A	8–11	314
10	A	15	343
11	A, (R)	15	107
12	A	6	308
13	A	30	78

^a A, anatase; R, rutile.

^b Reported by suppliers.

^c Specific surface area.

^d Not reported.

3.4. Photocatalytic decomposition of ammonia in aqueous suspensions of various commercial TiO₂ samples loaded with platinum

Various types of TiO₂ samples were supplied from The Catalysis Society of Japan. Their crystalline form, crystallite size and specific surface area are summarized in Table 1. Fig. 6 shows results of photocatalytic H₂ evolution from NH₃ in aqueous suspensions of these TiO₂ samples with Pt. Rutile samples (TIO-6) with Pt exhibited negligible activity. The results are attributed to a low level of the conduction band of the rutile phase that is insufficient for formation of H₂ (reduction of protons). In the cases of TiO₂ samples having an anatase structure, the TIO-10 sample with Pt exhibited the highest level of H₂ evolution and catalytic activities of the anatase samples were greatly dependent on the kind of TiO₂. These results indicate that selection of a commercial TiO₂ sample is important in photocatalytic H₂ formation from NH₃, although a clear correlation between photocatalytic activity and physical properties of commercial TiO₂ particles was not observed.

3.5. Hydrogen formation from methyl amine in an aqueous suspension of platinized TiO₂ particles

Fig. 7 shows time courses of evolutions of H₂ and N₂ in photocatalytic decomposition of methyl amine (30 μmol) in an aqueous suspension of Pt-loaded TiO₂ (P25) particles. Just after

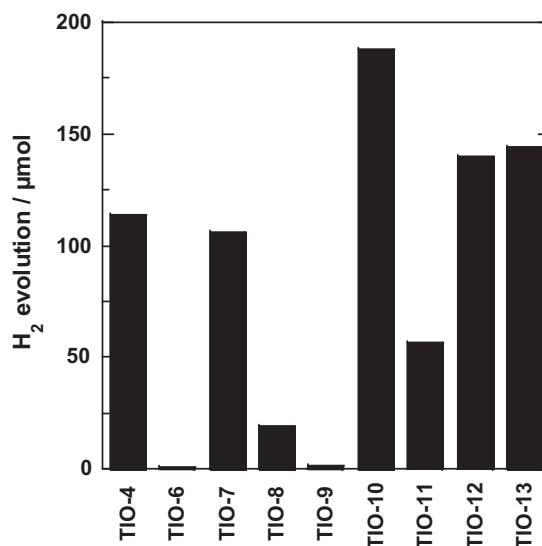


Fig. 6. Photocatalytic H₂ formation for 4 h from ammonia (500 μmol) in aqueous suspensions of various JRC-TiO samples loaded with platinum.

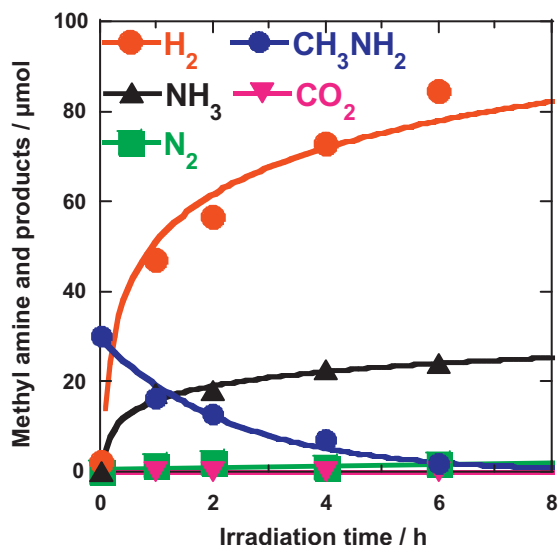


Fig. 7. Photocatalytic decomposition of methyl amine (30 μmol) in an aqueous suspension of platinum-loaded TiO_2 (P25) particles.

photoirradiation, the amount of methyl amine in the liquid phase decreased, while H_2 was evolved, indicating that methyl amine was decomposed under the conditions. As in the case of decomposition of NH_3 , the formation of O_2 was negligible (not shown in Fig. 7). The yield of N_2 was, however, very low in contrast to the case of NH_3 decomposition. Liquid phase analysis with ion chromatography revealed that nitrogen species remained in the liquid phase as NH_4^+ , indicating that cleavage of the C–N bond in methyl amine occurred but that the amino group was not decomposed under the present photocatalytic conditions. Gaseous CO_2 that originated in the methyl group of methyl amine was not detected. Evolution of CO_2 was observed when hydrochloric acid was injected to the liquid phase after the photoirradiation, although we did not determine the amount of CO_2 in detail, indicating that the methyl group was mineralized and CO_2 species stored in the liquid phase in the photocatalytic reaction. Fig. 8 shows changes in pH of the reaction suspension along with photoirradiation. Initial value of pH (10.8) was due to the basicity of methyl amine and the value decreased

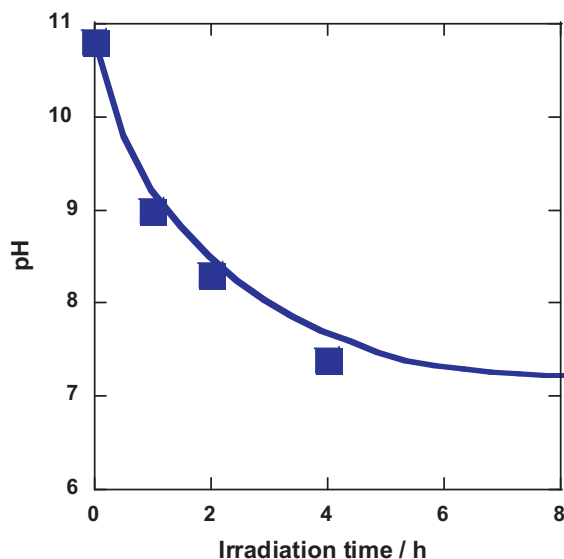
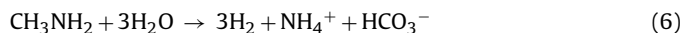


Fig. 8. Change in pH of an aqueous suspension of platinum-loaded TiO_2 particles in photocatalytic decomposition of methyl amine (30 μmol).

with prolongation of photoirradiation time. After reaching pH 7.4 with 4-h irradiation, the value was almost unchanged. The results showing that the value of pH of the reaction suspension decreased and converged to almost the neutral range despite NH_3 formation indicate that NH_3 was neutralized with a weak acid. Liquid-phase and gas-phase analyses showed that the nitrogen and carbon species formed by the photocatalytic reaction of methyl amine existed as NH_4^+ and hydrogencarbonate (HCO_3^-) and the reaction can be totally expressed as Eq. (6).



After irradiation for 6 h, 85 μmol of H_2 was formed that was almost in agreement with the amount (90 μmol) expected from the initial amount of methyl amine (30 μmol) (Fig. 7). Therefore, methyl amine can be used as the H_2 source in the photocatalytic reaction as well as NH_3 , although the amino group of methyl amine does not work as an H_2 source. Photocatalytic H_2 formation from methyl amine in the aqueous suspension also meant neutralization of methyl amine by salt formation between NH_3 and CO_2 .

4. Conclusions

We examined photocatalytic decomposition of NH_3 and methyl amine in aqueous suspensions of metal-loaded TiO_2 particles under a deaerated condition. NH_3 was decomposed to H_2 and N_2 stoichiometrically and side reactions such as deep oxidation of NH_3 to NO_2^- and NO_3^- did not occur under the present conditions. The rate of H_2 formation drastically changed depending on the type of co-catalyst, and Pt showed the greatest effect as a co-catalyst. The effect as a co-catalyst became smaller with increase in hydrogen over-voltage of the co-catalyst metal. The effect of pH of the reaction suspension was also examined, and the largest rate of H_2 evolution was obtained when the photocatalytic reaction was carried out at pH 10.7 with neither an acid nor a base being added to the suspension. Various kinds of TiO_2 samples were supplied from The Catalysis Society of Japan and used for decomposition of NH_3 after platinization. Catalytic activities of the TiO_2 samples were greatly dependent on the kind of TiO_2 . Rutile samples with Pt exhibited negligible activity due to the low level of the conduction band of the rutile phase that is insufficient for formation of H_2 (reduction of protons).

Methyl amine was decomposed in an aqueous suspension of platinum-loaded TiO_2 particles under a deaerated condition, and H_2 was evolved. The methyl group of methyl amine was mineralized and the carbon remained as hydrogencarbonate in the suspension. The amino group was eliminated from methyl amine and remained as NH_4^+ together with HCO_3^- without being decomposed to H_2 and N_2 , probably due to high stability of NH_4^+ against photocatalysis. Photocatalytic reaction of methyl amine under the present conditions was totally expressed as: $\text{CH}_3\text{NH}_2 + 3\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{NH}_4^+ + \text{HCO}_3^-$ and also meant neutralization of methyl amine in an aqueous solution.

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References

- [1] A.L. Linsebigler, G.Q. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735.
- [2] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
- [4] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49.
- [5] M.D. Hernandez-Alonso, F. Fresno, S. Suarez, J.M. Coronado, Energy Environ. Sci. 2 (2009) 1231.

- [6] X. Chen, S. Shen, L. Guo, S.S. Mao, *Chem. Rev.* 110 (2010) 6503.
- [7] K. Maeda, K. Domen, *J. Phys. Chem. Lett.* 1 (2010) 18.
- [8] S. Sato, J.M. White, *Chem. Phys. Lett.* 72 (1980) 83.
- [9] A. Kudo, A. Tanaka, K. Domen, K. Maruya, K. Aika, T. Onishi, *J. Catal.* 111 (1988) 67.
- [10] S. Tabata, H. Nishida, Y. Masaki, K. Tabata, *Catal. Lett.* 34 (1995) 245.
- [11] S.-C. Moon, H. Mametsuka, E. Suzuki, M. Anpo, *Chem. Lett.* (1998) 117.
- [12] S.-C. Moon, H. Mametsuka, E. Suzuki, Y. Nakahara, *Catal. Today* 45 (1998) 79.
- [13] H. Kato, K. Asakura, A. Kudo, *J. Am. Chem. Soc.* 125 (2003) 3082.
- [14] K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, *J. Am. Chem. Soc.* 127 (2005) 8286.
- [15] T. Kawai, T. Sakata, *J. Chem. Soc. Chem. Commun.* (1980) 694.
- [16] T. Kawai, T. Sakata, *Nature* 286 (1980) 474.
- [17] T. Kawai, T. Sakata, *Chem. Lett.* (1981) 81.
- [18] S.-I. Nishimoto, B. Ohtani, T. Kagiya, *J. Chem. Soc. Faraday Trans. 1* (81) (1985) 2467.
- [19] R.M. Navarro, M.C. Sa'nchez-Sa'nchez, M.C. Alvarez-Galvan, F. del Valle, J.L.G. Fierro, *Energy Environ. Sci.* 2 (2009) 35.
- [20] D.I. Kondarides, V.M. Daskalaki, A. Patsoura, X.E. Verykios, *Catal. Lett.* 122 (2008) 26.
- [21] V.M. Daskalaki, D.I. Kondarides, *Catal. Today* 144 (2009) 75.
- [22] K. Shimura, H. Yoshida, *Energy Environ. Sci.* 4 (2011) 2467.
- [23] H. Kominami, Y. Takada, H. Yamagiwa, Y. Kera, M. Inoue, T. Inui, *J. Mater. Sci. Lett.* 15 (1996) 197.
- [24] H. Kominami, M. Kohno, Y. Takada, M. Inoue, T. Inui, Y. Kera, *Ind. Eng. Chem. Res.* 38 (1999) 3925.
- [25] T. Sakata, T. Kawai, *Chem. Phys. Lett.* 80 (1981) 341.
- [26] H. Kominami, A. Furusho, S.-Y. Murakami, H. Inoue, Y. Kera, B. Ohtani, *Catal. Lett.* 76 (2001) 31.
- [27] H. Kominami, T. Matsuura, K. Iwai, B. Ohtani, S.-I. Nishimoto, Y. Kera, *Chem. Lett.* (1995) 693.
- [28] H. Kominami, S.-Y. Murakami, Y. Kera, B. Ohtani, *Catal. Lett.* 56 (1998) 125.
- [29] B. Ohtani, K. Iwai, H. Kominami, T. Matsuura, Y. Kera, S.-I. Nishimoto, *Chem. Phys. Lett.* 242 (1995) 315.
- [30] H. Kominami, J.-I. Kato, M. Kohno, Y. Kera, B. Ohtani, *Chem. Lett.* (1996) 1051.
- [31] B. Ohtani, R. Bowman, D.P. Colombo Jr., H. Kominami, H. Noguchi, K. Uosaki, *Chem. Lett.* (1998) 579.
- [32] H. Kominami, S.-Y. Murakami, M. Kohno, Y. Kera, K. Okada, B. Ohtani, *Phys. Chem. Chem. Phys.* 3 (2001) 4102.
- [33] H. Kominami, S.-Y. Murakami, J.-I. Kato, Y. Kera, B. Ohtani, *J. Phys. Chem. B* 106 (2002) 10501.
- [34] S.-Y. Murakami, H. Kominami, Y. Kera, S. Ikeda, H. Noguchi, K. Uosaki, B. Ohtani, *Res. Chem. Intermed.* 33 (2007) 285.